Removal of Zn(II) Ion from Aqueous Solution using Activated Carbon Prepared from Rice Husk Treated with Sodium Hydroxide

by

Muhammad Hanifi bin Che Ibrahim

Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2012

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CERTIFICATION OF APPROVAL

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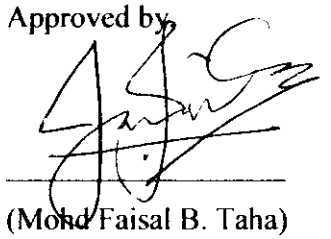
Approved by,



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TRONOH, PERAK
JANUARY 2012

CERTIFICATION OF ORIGINALITY

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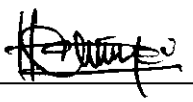

MUHAMMAD HANIFI BIN CHE IBRAHIM

ABSTRACT

The study of rice husk as potential activated carbon as a low-cost adsorbent to remove zinc (Zn) from Zn(II) ion solution was investigated. Raw rice husk as an agricultural waste was chosen for this project due to its huge amount of production during milling activities. The scope of this study covers from preparation of the rice husk activated carbon (RHAC) to the experimental works for removal of Zn(II) ion from aqueous solution. The preparation involves three stages which are grinding to size of 63 μm, digestion and carbonization. 63 μm raw rice husks were digested with 1.0 M sodium hydrochloride (NaOH) solution for 24 hours. The treated rice husks were then carbonized at 650°C for 1 hour in order to remove volatile organic constituents leaving behind highly porous carbonaceous materials. Once the activated carbon was prepared, mixing process with Zn(II) ion solution at various contact time ranging from 5 to 180 minutes was carried out to study the adsorption capacity. In this study, pores development in rice husk was analyzed using FESEM for each stage. Other analyses on rice husk activated carbon were also conducted using BET Surface Area Analyzer, Fourier Transmitter Infrared Spectroscopy (FTIR), CHN Elemental Analyzer, X-ray Diffraction (XRD) and Energy-Dispersive X-ray Spectroscopy (EDX) for characterization study. The adsorption capacity towards metal ion was determined using Atomic Adsorption Spectroscopy (AAS). The results obtained from the adsorption study showed that rice husk has a potential to be converted to adsorbent for the removal of heavy metals.

ACKNOWLEDGEMENT

In the name of ALLAH S.W.T, the most merciful and compassionate, praise to ALLAH, he is the almighty, eternal blessing and peace upon the Glory of the Universe, our beloved Prophet Muhammad (S.A.W), and his family and companions.

The author would like to express his gratitude towards his supervisor, Mr. Mohd Faisal Taha for all the support, ideas and advice that has been given towards the author for the duration of this final year project being conducted. His sincere guidance, supervision and dedication have really helped the author in ensuring the project in successful manner.

Special thanks as well to all lab technicians for their guidance towards the author for the period of project conducted especially Mr. Asnizam, technician of Block 3, Mr. Fazli, technician of Block 5, Mr. Mahfuzrazi, technician of Block 17 and Mr. Syamil, technician of Block P. Without their help, the author would be dealing with hard situation in order to ensure the smoothness of experiments to be performed for the entire duration of this project.

This special thanks and appreciation are also dedicated to all colleagues and my parents who are directly and indirectly contributed towards the success of this project. With the full cooperation from various people above, the author has successfully achieved the objective of this project.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND OF STUDY

Heavy metals discharged into the environment are increasing due to rapid industrialization and have created a major global concern. Metal ions such as cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc., (Wan Ngah & Hanafiah, 2008).

Different from organic waste that are biodegradable, heavy metals are non-biodegradable and they can be accumulated in living tissues and subsequently causing various diseases and disorders. Therefore, heavy metals must be removed before discharge. Table 1 below shows the Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, in Malaysia with selected parameter limits of effluent of heavy metals.

Table 1: Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, Malaysia: Selected parameter limits of effluent of Standards A and B (Department of Environment, DOE, Malaysia)

Parameters, mg/l	Standard	
	A*	B
Cadmium	0.01	0.02
Zinc	1.0	1.0
Copper	0.20	1.0
Nickel	0.2	1.0
Lead	0.10	0.50
Mercury	0.005	0.05
Chromium, Trivalent	0.2	1.0

*This standard applies to the industrial and development projects which are located within catchment areas (areas upstream of surface or above sub-surface water supply intakes, for the purpose of human consumption including drinking).

The main techniques to remove heavy metal ions from wastewater streams include ion-exchange chromatography, reverse-osmosis, chemical precipitation, and adsorption (Srivastava, Mall, & Mishra, 2008). These technologies are not economically feasible for such industries due to its relatively high costs. Therefore, new alternatives of low cost method are studied to achieve effective and economically viable method of heavy metal ions removal in wastewater.

Adsorption on activated carbon has been recognized to be one of the most efficient and economic method for wastewater treatment process for recent years. Activated carbon can be made from agricultural wastes such as oil palm nut shell, rice husks, olive-waste cakes, palm seeds, guava seeds and corncobs (Rahman, Ismail, & Osman, 2000). These materials are exposed to chemical or physical treatments for studies on their adsorption capacity by analyzing the physical properties of the subsequent product. Plant wastes are inexpensive as they have no or very low economic value. Some of the advantages of using plant wastes for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, freely available and easy regeneration (Wan Ngah & Hanafiah, 2008).

The manufacturing process of activated carbon consists of two phases; carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons from the raw material, as well as to drive-off any gases generated. The carbonization process is completed by heating the material at 400°C to 600°C in an oxygen-deficient atmosphere that cannot support combustion, usually in nitrogen-blowing furnace.

The carbonized particles are activated by exposing them to an activating agent, such as steam at high temperature. The steam burns off the decomposition products from the carbonization phase to develop porous, three dimensional graphite lattice structures. The size of the pores developed during activation is a function of the time that they are exposed to the steam. Longer exposure times result in larger

pore sizes. The most popular aqueous phase carbons are bituminous based because of their hardness, abrasion resistance, pore size distribution and low cost but their effectiveness needs to be tested in each application to determine the optimal product.

Many developing countries are known to dispose their agricultural waste due to inadequate technology or capacity to manipulate the materials. Since rice husk have the capability of handling environmental problem caused by heavy metal ions wastewater system, research in converting rice husks into activated carbon should be significantly considered. Therefore, studies on rice husks as a low-cost adsorbent should be done on its beneficial potential to remove heavy metal ions in wastewater.

According to the statistics compiled by the Malaysia Ministry of Agriculture (MOA, 2008) and Department of Statistics, Malaysia (DOS, 2010), production of paddy is 2,375,000 tonnes, 2,384,000 tonnes and 2,510,000 tonnes for 2007, 2008 and 2009 respectively. Chuah et al. (2005) stated that rice husk takes account for about 20% of the whole rice and that means more than 400,000 tonnes of rice husk produced annually in Malaysia.

Rice husks are rich in organic materials and silica which can be converted into activated carbon for heavy metal removal. Rice husks abundant as an agricultural waste has lead to many researches to transform it into activated carbon or use it naturally as it has good adsorptive property in removal of metal ions and dyes as reported by the researchers (Chuah et al., 2005).

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

Heavy metals are toxic pollutants that can harm living creatures and human beings. Differs from other toxic pollutants, metals are non-biodegradable and can accumulate in living organisms, causing various diseases and disorders (Chuah et al., 2005). Increasing disposal of heavy metals into the environments has become serious problem since the beginning of industrialization era because heavy metals cannot be treated via domestic wastewater treatment.

Metals such as zinc are known to be essential to plants, humans and animals, but they can also have adverse effects if their concentration in water exceeds certain threshold values. Zn(II) ion is one of the most important pollutants for surface and ground water. Because of its toxicity and non-biodegradability, zinc containing liquid and solid wastes is considered as a hazardous waste (El-Said, Badawy, Abdel-Aal and Garamon, 2010). Hence, it is essential to remove Zn(II) ion from industrial wastewaters before discharging into natural water resources.

In most countries that produced rice, the husks as an agricultural waste from rice processing are usually burnt in situ, generating carbon dioxide (CO_2) and various compounds toxic such as nitrogen oxides, volatile organic compounds (VOCs), carbon monoxide and suspended particles which are harmful to the environment.

1.2.2 Significance of the Project

Adsorption is recognized to be an efficient and economically feasible method to remove heavy metal ions wastewater compared to other existing methods including ion exchange, membrane separation and precipitation. Activated carbon from cheap and readily available sources like rice husks could be employed for the removal of zinc and other toxic heavy metal ions from wastewater. Besides, rice

husks are one of the agricultural wastes which are abundant in Malaysia. Thus, a study is proposed to develop economically feasible adsorbent from rice husks, which is considered as low-cost adsorbent. Since the main components of the rice husks are carbon and silica, it has the potential to be used as an adsorbent. The activated carbons of rice husks contain silica with high porosity and large surface area which has potential for adsorption of heavy metals.

However, the rice husks need to be treated so that the activated carbon can be produced. The utilization of untreated plant wastes as adsorbents can also bring several problems such as low adsorption capacity, high COD and BOD as well as TOC due to release of soluble organic compounds contained in the plant materials (Nakajima and Sakaguchi, 1990).

1.3 OBJECTIVE AND SCOPE OF STUDY

The main objectives of this project are:

- To study the potential of rice husk as an activated carbon for adsorption of Zn(II) ions from aqueous solutions
- To study the pore development of rice husk throughout the preparation processes
- To determine the adsorption capacity of rice husk activated carbon digested with sodium hydroxide (NaOH)

The scope of study for this project will cover from preparation of rice husk activated carbon digested with NaOH, characteristic study of rice husk samples throughout the preparation stages and determination of the adsorption capacity. Observation of the results as well as proper documentation will be done in order to achieve the mentioned objective.

1.3.1 The Relevancy of the Project

Activated carbon prepared from treated rice husks could be used as an alternative adsorbent for the removal of heavy metal ions from industrial wastewater. The removal of heavy metal ions from wastewater is very significant to be safely used for daily activities and avoid any harm towards environment. The use of commercial activated carbon such as graphite as an adsorbent is limited, especially in developing countries because of its relatively high cost and the difficulties associated with its regeneration. Thus, using agricultural wastes which is rice husks in this study could be the cheaper alternative of commercial activated carbon for removal of Zn(II) ions by adsorption process.

1.3.2 Feasibility of the Project within Scope and Time Frame

The raw rice husks were readily available for the study, obtained from local rice mills factory. The rice husks need to be cleaned with distilled water, grinding and sieving to 63 μm size before treating with NaOH. Later, the rice husks will undergo carbonization process to prepare the activated carbon. Several adsorption studies were performed to determine the adsorption capacity of the activated carbon. All the equipment and chemicals required for this project are available in the Chemical Engineering Department Laboratory or other department laboratory that can be borrowed for use. Since all the resources are provided, this project can be considered a feasible project within the time frame given.

CHAPTER 2: LITERATURE REVIEW

Several studies of using rice husk to remove heavy metal in aqueous solution via adsorption have been conducted by researchers around the world. There are the experiments using untreated rice husk and treated rice husk performed to validate the adsorption capacity. Basically, treated rice husk that have been transformed into activated carbon is more capable of being used as adsorbent rather than the untreated one. Table 2 below and 3 on the next page show the typical composition and chemical compositions of rice husk and reported values on their physicochemical characteristics (Chuah et al., 2005).

Table 2: Typical composition of rice husk

Composition	Percent
Cellulose	32.34
Hemicellulose	21.34
Lignin	21.44
Extractives	1.82
Water	8.11
Mineral ash	15.05
Chemical composition in mineral ash:	
SiO_2	96.34
K_2O	2.31
MgO	0.45
Fe_2O_3	0.2
Al_2O_3	0.41
CaO	0.41
K_2O	0.08

Wan Ngah and Hanafiah (2007) reviewed that untreated plant wastes as adsorbents are unlikely to be used because they can bring several problems such as low adsorption capacity, high chemical oxygen (COD), biological oxygen demand (BOD) and total organic carbon (TOC). Thus, this made treated plant wastes such as rice husk that have been treated physically and chemically as more reliable adsorbents.

Table 3: Reported physiochemical characteristics of rice husk

Characteristics	Values
Bulk density (g/ml)	0.73
Solid density (g/ml)	1.5
Moisture content (%)	6.62
Ash content (%)	45.97
Particle size (mesh)	200-16
Surface area (m^2/g)	272.5
Surface area acidity (meq/gm)	0.1
Surface basicity (meq/gm)	0.45

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As stated by Sud, Mahajan and Kaur (2008), the major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, regeneration of biosorbents and possibility of metal recovery. Since agricultural wastes such as rice husk are available abundantly in Malaysia, utilization as activated carbon for heavy metal removal is economically reliable. Table 4 below shows the maximum zinc adsorption capacities for rice husk that have been reported by other researchers (Chuah et al., 2005).

Table 4: Reported maximum zinc adsorption capacities for rice husk

Researchers	Capacities (mg/g)
Marshall et al., 1993	0.75
Mishra et al., 1997	26.94 (20°C)
	28.25 (30°C)
	29.69 (40°C)
	30.80 (50°C)
Munaf and Zein, 1997	0.173

Different kinds of modifying agents have been used and tested for the treatments such as base solutions, mineral and organic acid solutions, organic compounds, oxidizing agent, dye and many others (Wan Ngah & Hanafiah, 2008). Commonly used chemical for treatment of rice husk are hydrochloric acid, sodium hydroxide, sodium carbonate, epichlorohydrin and tartaric acid.

In a study conducted by An, Guo, Zou, Zhu and Wang (2011), they used sodium carbonate, a type of base to leach out silica in order to increase high surface areas. They concluded that, the optimal experimental conditions are 2:1 of impregnation ratio between carbon residue and iodine adsorption capacity with 850°C of activation temperature.

Treatment using base such as KOH and NaOH of pyrolysed rice husk followed by activation at 650-850 °C results in activated carbon with extremely high surface areas (1413-3014 m^2/g) as reported by Guo et al., (2002). Thus, it is most likely the best to treat rice husk chemically using base in order to increase the pore in the rice husk.

2.1 ACTIVATED CARBON

Activated carbon, also called activated charcoal or activated coal is a form of carbon that has been processed to make it extremely porous and thus have a very large surface area available for adsorption or chemical reactions.

The word *activated* in the name is sometimes replaced with *active*. Due to its high degree of micro-porosity, just 1 gram of activated carbon can have surface area in excess of 500 m^2, with 1500 m^2 being readily available. Sufficient activation for useful applications may come solely from the high surface area, though further chemical treatment often enhances the adsorbing properties of the material.

Activated carbon is useful in drinking water treatment because it acts as an adsorbent and can effectively remove particles and organics from water. These organics are of great concern in water treatment because they react with many

disinfectants, especially chorine, and causing the formation of disinfection-by-products, DBP's.

Activated carbon adsorption process through 3 basic steps:

i. Substances adsorbed to the exterior of the carbon granules.
ii. Substances move into the carbon pores.
iii. Substances adsorbed to the interior walls of the carbon.

2.1.1 Properties of Activated Carbon

The properties of a good activated carbon are referred to:

i. Its large surface area
ii. A high degree of surface activity
iii. Universal adsorption effect
iv. Favorable pore size as an access route to the internal surfaces
v. Enhanced mechanical strength

Under an electron microscope, the high surface area structures of activated carbon are revealed. Individual particles are intensely convoluted and display various kinds of porosity; there may be many areas where flat surfaces of graphite-like material run parallel to each other, separated by only a few nanometers or so. There micropores provide superb conditions for adsorption to occur, since adsorbing material can interact with many surfaces simultaneously. Physically, activated carbon binds materials Van der Waals force or London dispersion force.

The reason that activated carbon is such an effective adsorbent material is due to its large number of cavernous pores. These provide a large surface area relative to

the size of the actual carbon particle and its visible exterior surface. An approximate ratio is 1 gram = 100 m^2 of surface area.

2.1.2 Chemical Structures of Activated Carbon

Carbon materials are activated by a series of process which include:

i. Removal of all water (dehydration)
ii. Conversion of the organic matter to elemental carbon, driving off to the non-carbon portion (carbonization)
iii. Burning off tars and pore enlargement (activation)

The basic structural unit of activated carbon is closely approximated by the structure of pure graphite. The graphite crystal is composed of layers of fused hexagons held by weak Van der Waals forces. The layers are held by carbon-carbon bonds.

Activated carbon is a disorganized form of graphite, due to impurities and the method of preparation (activation process). The structure developed is a function of the carbonization and activation temperatures. In terms of pore structure, the adsorbent pores can be divided into three basic classes: macropores (> 1000Å), transitional or mesopores and micropores (< 10Å). The macropores do not add appreciably to the surface area of the carbon, but provide a passageway to the particle interior and the micropores. The micropores are developed primarily during carbon activation and result in the large surface area for adsorption to occur.

2.2 FACTORS AFFECTING ADSORPTION

2.2.1 Particle Size

The adsorption capacity of rice husk depends very much on the surface acitivites, i.e., specific surface area available for solute surface interaction, which is accessible to solute. It is expected that with larger surface area, adsorption capacity will be increased because smaller particle size increases the adsorption capacity. Munaf and Zein (1997) reported that metal ions adsorbed decreases when the size of rice husk particle increases. Similar trends have been reported by Wong et al. Adsorption as surface phenomenon, smaller particle size will offer comparatively larger surface areas and higher adsorption will occur.

2.2.2 pH of Activation Agent

At high pH, metal ion may be forced to bind to low affinity ligands such as hydroxyl and carboxyl group but at low pH, the binding may occur through high affinity ligands only (Michael Horsfall Jr. et al., 2004). This is an indication that the degree of ionization on the biomass surface is pH dependent (Michael Horsfall Jr. et al., 2004) which later affect the metal adsorption activities.

Bhattacharya et al (2006) reported that removal efficiency was found to be highly dependent on hydrogen ion concentration that present in solution. At low pH, due to high positive charge density due to protons on the surface sites, electrostatic repulsion will be high during uptake of metal ions resulting in lower removal efficiency. With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption. At higher pH values, OH ions compete for Zn(II) with the active sites on the surface of the adsorbents (Kalyani et al., 2003).

2.2.3 Carbonization Time of Rice Husk

It is reported that activity of adsorption decreases as carbonization time increases. This is probably due to the thermal destruction of pores structure as the carbonization time increases. It may also be due to formation of ash, which may block the pores entrance (Shasanka Sekhar, 2009).

An increased in the burning time increased the amount of silica but decreased the amount of carbon content significantly. The decrease of carbon content will predictably cause the decrease of the porosity of the adsorbent. This is expected since at longer times, more carbon are converted to silica (Daffalla, Mukhtar, & Shaharun, 2010).

2.2.4 Carbonization Temperature of Rice Husk

The purpose of carbonizing the rice husk is to impart thermal decomposition to it, thus eliminating non-carbon species and fixed the carbon mass as well as the basic carbon structure. Generally, the quality and yield of the carbonized activated carbon are affected by numerous parameters which are:

- The rate of heating
- The heating final temperature
- The soaking time at the final temperature
- Nature and physical state of the raw material

Low heating rate during pyrolysis results in lower volatilization and higher char. These occur due to the increased dehydration and better stabilization of the polymeric components.

At the first stage of carbonization, the structure of the activated carbon is made of small planar aromatics rings which are randomly oriented. As the heat treatment temperature increases, the random structure will start to be arranged in parallel. The basic microstructure was formed by 500°C, although some of these pores are blocked by the pyrolysis products and could be available only when high temperature treatment is given.

2.2.5 Contact Time of Adsorption Activities

The contact time affect metal adsorption on rice husk activated carbon as the contact time increases, the metal ion adsorbed will also increase (Guo et al., 2000). About three hours of adsorption, the rate of adsorption will become constant which means the process has achieved an equilibrium condition (Montaher et al., 2005). However, the fast kinetics between rice husk and the metal depends on the analytical speed and the removal efficiency. Therefore, this factor need to be considered and must be made constant as the effect of contact time is tested.

CHAPTER 3: METHODOLOGY

3.1 PROCEDURES

The overall methodology of this study can be divided into four major parts:

i. Preparation of raw rice husk
ii. Treatment of raw rice husk
iii. Carbonization of treated rice husk
iv. Adsorption study

The first three parts stated above are the methods that involved in preparing rice husk-based activated carbon. The final part of the experiment is performing adsorption study with zinc chloride, $ZnCl_2$ as the adsorbate. From the study, adsorption activity of prepared activated carbon can be observed, thus the capability of rice husk to adsorb Zn(II) ions can be proven. Raw rice husk were obtained from local rice mills factory situated in Semanggol, Perak to be used as feedstock for this study.

3.1.1 Preparation of Raw Rice Husk

Cleaning and drying of rice husk are done before obtaining the desired size of rice husk. The brief procedures of this process are stated below:

i. About 500 g of raw rice husk was washed with tap water several times to remove any adhering materials.
ii. Rice husk was then dried in the oven at 100°C for 24 hours.
iii. The dried rice husk was grinded using mortar grinder.
iv. Grinded rice husk was then sieved using sieve tray sized 63 μm to obtained 63 μm size of rice husk.

3.1.2 Treatment of Raw Rice Husk

1.0 M of sodium hydroxide (NaOH) was used as activation agent for the rice husk treatment process. The required NaOH was prepared by dissolving 40 g of NaOH pellets in 1 L of distilled water. The ratio of rice husk to the digestion agent was 1:10 where rice husk is in unit of gram (g) while digestion agent is in unit of millimeter (ml).

The procedures for treatment of rice husk are as follows:

i. 1.0 M NaOH was prepared.
ii. 50 g of raw rice husk size 63 μm was digested with 500 ml of 1.0 M NaOH in 600 ml beaker.
iii. Beaker containing sample was sealed using aluminum foil.
iv. After 24 hours, the digested sample was filtered was washed with excessive deionized water until the filtrate is free from base (pH range from 6 to 7).
v. Sample was placed in beaker for drying process in an oven at 100°C for 24 hours.
vi. Then, the sample was weighed.

*Preparation of NaOH is to be conducted in fume hood for safety reason.

3.1.3 Carbonization of Treated Rice Husk

The treated rice husk are carbonized to impact thermal decomposition to it thus eliminating non-carbon species and fixed the carbon mass as well as the basic carbon structure. A total of about 5 grams of treated rice husk are carbonized.

The steps of carbonization are as follows:

i. About 5 g of treated of rice husk was weighed.
ii. Aluminum foil was used to wrap the treated rice husk.

iii. Wrapped samples were placed into the crucibles and crucible lids were used to close crucibles to minimize the effect of oxidization.

iv. The crucible containing rice husk was put in the furnace when the temperature reaches nearly 650°C.

v. After carbonizing for 1 hour, furnace temperature was reduced to 30°C.

vi. Samples were taken out once the furnace has reached the desired temperature.

vii. After that, samples were weighed and percentage loss of weight was calculated.

3.1.4 Adsorption Study

The purpose of adsorption process is to observe the adsorption activities. Adsorption study was carried out by mixing 0.1 g of sample in 15 ml of 100 ppm metal ion solution. Contact time was varied ranging from 5 min to 180 min. Samples were then filtered to get the filtrate before analyzed using Atomic Adsorption Spectrophotometer (AAS).

Below are the procedures conducted to study the adsorption capacity of rice husk-based activated carbon using AAS.

i. 15 ml of 100 ppm Zn^{2+} was prepared and mixed with 0.1 g of carbonized rice husk in the Wheaton bottle.

ii. Wheaton bottle was placed in stem block and left for stirring at 850 rpm and at room temperature for 5 minutes.

iii. The solutions were then filtered and the filtrate is analyzed using AAS to check the metal concentration left in the filtrate.

iv. Steps 1 to 3 were also conducted for various contact time ranging from 15, 30, 45, 60, 90, 120, 150 and 180 minutes.

v. Graphs were plotted to observe the effect of parameters varied on the adsorption activities.

3.1.5 Analyses

Samples before and after extraction study are analyzed using several equipments namely Field Emission Scanning Electron Microscope (FESEM), Fourier Transform Infrared (FTIR), CHN Elemental Analyzer, X-ray Diffraction (XRD), Energy-Dispersive X-ray Spectroscopy (EDX/EDS), and Atomic Absorption Spectrometer (AAS). Below is the list of samples (for reference) which were sent for analysis.

Table 5: List of Samples for Analysis Study

No.	Sample Name & Description	Label
1.	Raw Rice Husk (63 μm)	RRH
2.	Treated Rice Husk	TRH
3.	Carbonized Rice Husk	CRH
4.	Used Carbonized Rice Husk	UCRH

Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. It produces images of high resolution, which means that closely spaced features can be examined at high magnification. Preparation of the sample is relatively easy since SEM only required the sample to be conductive. The development of pores can be easily observed due to the combination of higher magnification, larger depth of focus and great resolution.

Figure 1: FESEM

BET Surface Area Analyzer

BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material.

Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FTIR) is the preferred method of infrared spectroscopy. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. The size of the peaks in the spectrum is a direct indication of the amount of material present. The main purpose of performing FTIR analysis in this study is to identify the functional group of the samples.

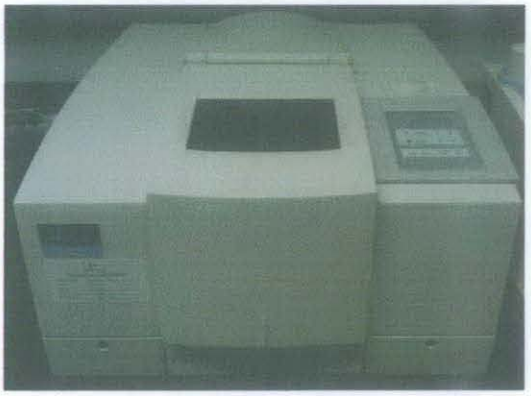

Figure 2: FTIR

CHN Elemental Analyzer

CHN Elemental Analyzer can provide a mean for the rapid determination of carbon, hydrogen and nitrogen in organic matrices and other types of materials. CHN Elemental Analyzer is performed to provide carbonate and organic carbon and to get some idea of the composition of the organic matter.

Figure 3: CHN Elemental Analyzer

X-ray Diffraction (XRD)

The principal function of XRD is to measure the diffraction beam intensity and the d-spacings of crystalline materials, which however has been developed to determine many structural properties. In this study, XRD is conducted to investigate the crystalline and amorphous phases of the carbon samples. XRD experiments are performed with 2Θ values ranging from 2° to 80°.

Energy-Dispersive X-ray Spectroscopy (EDX)

Energy-Dispersive X-ray Spectroscopy (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles.

Atomic Absorption Spectrometer (AAS)

Atomic Absorption Spectrometer (AAS) is analytical equipment used in research works as it is the only equipment that can give definite reading of the metal ions' concentration. AAS works by providing the accurate quantitative analyses for metals in water, sediment soils or rock. In this study, the purpose of using AAS is to determine the final concentration of the metal ion in the filtrate.

Figure 4: AAS

3.2 EQUIPMENTS AND CHEMICALS

Lab equipments needed in this project are as follows:

Table 6: List of equipments

No.	Equipment	Quantity	Remarks
1.	FESEM	As per requirement	
2.	BET	As per requirement	
3.	FTIR	As per requirement	
4.	CHN Elemental Analyzer	As per requirement	
5.	XRD	As per requirement	
6.	EDX	As per requirement	
7.	AAS	As per requirement	Max: 4 ppm of Zn
8.	Electrical siever	As per requirement	63 μm
9.	Mortar grinder	As per requirement	
10.	Oven	As per requirement	
11.	Furnace	As per requirement	With nitrogen flow
12.	pH meter	As per requirement	Calibrated
13.	Stem block	As per requirement	
14.	Volumetric flask	As per requirement	1 L

The chemicals involved in this project are listed below:

Table 7: List of chemicals required

No.	Chemical	Quantity	Remarks
1.	Sodium Hydroxide, NaOH	As per requirement	Pellets form
2.	Zinc Chloride. $ZnCl_2$	As per requirement	Adsorbate
3.	Distilled water	As per requirement	
4.	Deionized water	As per requirement	

CHAPTER 4: RESULTS AND DISCUSSIONS

This chapter presents the finding and discussion from the result obtained during lab work of preparation of rice husk activated carbon (RHAC) and the adsorption study of Zn(II) ions using RHAC.

4.1 PREPARATION OF RAW RICE HUSK

During the preparation process, rice husk was cleaned using tap water. Based on observation, a lot of impurities were floating on water surface while most of rice husk stay at the bottom. Main purpose of cleaning process is to get rid of any foreign substances that may contaminate the rice husk composition. After grinding and sieving, amount of 63 μm rice husk collected was 50.05 g for the first batch. The color of 63 μm raw rice husk was dull brown.

4.2 TREATMENT OF RAW RICE HUSK WITH SODIUM HYDROXIDE

Using ratio 1:10, 50 g of raw rice husks were mixed with 500 ml NaOH. This treatment of rice husk was done for 24 hours. Observations on no color change and mass of the rice husk was recorded.

Table 8: Observation results of treated rice husk

	Color	**Weight (g)**
Before	Dull brown	50.05
After treatment	Dull brown	6.00
Weight loss (After treatment –Before)		44.05

Final pH for treated rice husk after washing with excessive distilled water was 7.04.

4.3 CARBONIZATION OF TREATED RICE HUSK

The carbonization process was conducted at 650°C with nitrogen flow as inert gas. A 5.094 gram of treated rice husk was carbonized at the desired temperature for the first batch. The color of rice husk samples turned into dark black. The weight of the sample decreased after carbonization process due to the lost of volatile matter as the process undergo rapid heating (Rahman et al, 2000). The results obtained are tabulated in Tables 9 and 10.

A summary of carbonization result is shown below.

Table 9: Observation result of carbonized rice husk

Temperature (°C)	Color		Weight (g)	
	Before Carbonization	After Carbonization	Before Carbonization	After Carbonization
650	Dull brown	Dark black	5.094	1.672

Table 10: Percentage weight loss after carbonization

Temperature (°C)	Color		Percentage Weight Loss (%)
	Before Carbonization	After Carbonization	
650	Dull brown	Dark black	67.18

Weight of samples after carbonization was reduced due to elimination of certain elements such as nitrogen and oxygen in the rice husk during carbonization process. Removal of volatile component is necessary to produce a better activated carbon.

4.4 ANALYSES

4.4.1 Field Emission Scanning Electron Microscope (FESEM)

Three samples of rice husk were analyzed using Field Emission Scanning Electron Microscope (FESEM) which are raw rice husk, rice husk treated with 1.0 M sodium hydroxide and carbonized rice husk at 650°C.

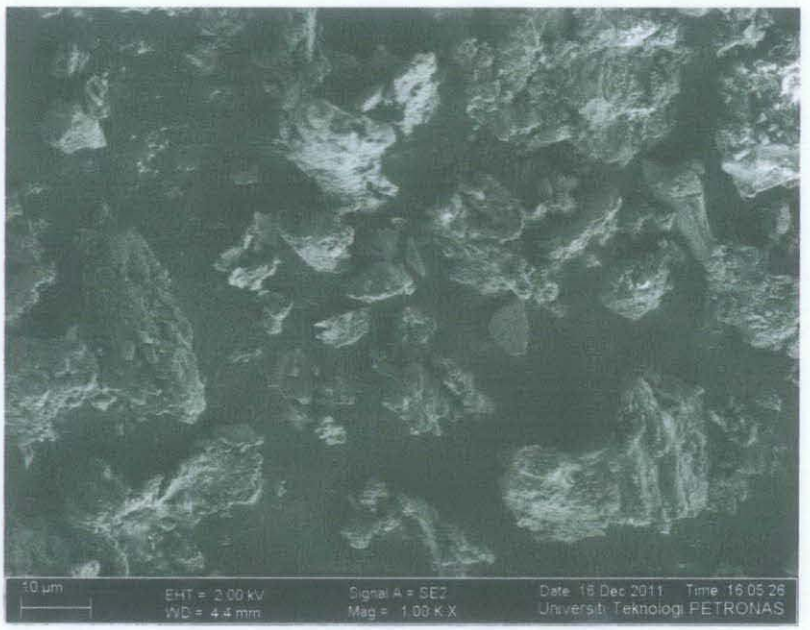

Figure 5: Raw rice husk (1000 times magnification)

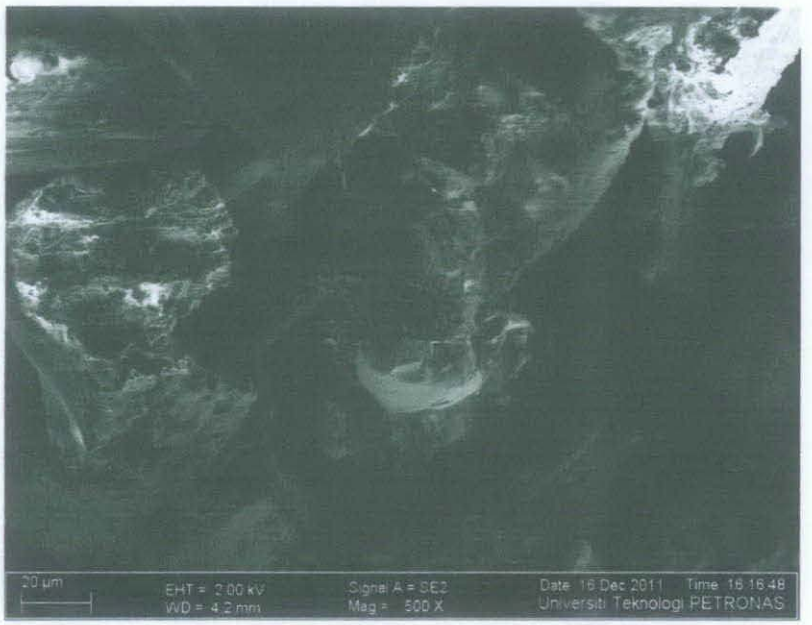

Figure 6: Raw rice husk treated with 1.0 M NaOH (500 times magnification)

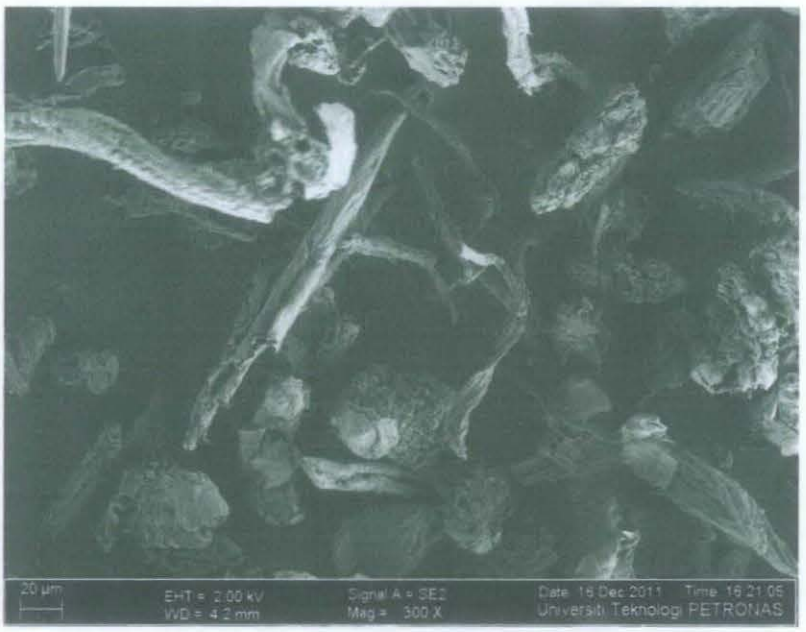

Figure 7: Carbonized rice husk at 650°C (300 times magnification)

The FESEM micrographs of raw rice husk, treated rice husk and carbonized rice husk are shown in Figure 5-7. Different morphology was obtained for every carbon sample as the pores of rice husk were developed throughout processes, i.e., treatment and carbonization process. Figure 5 shows that there is no evidence of pores while obvious pores can be observed on the rice husk that has been treated with 1.0 M sodium hydroxide as shown in Figure 6. As compared to raw rice husk, it can be seen that the development of pores has occurred after rice husk going through treatment process.

4.4.2 BET Surface Area Analyzer

Table 11 presented the reported BET surface area (S_{BET}), pore volume and average pore diameter of carbonized rice husk.

Table 11: A summary of the porous structure of carbonized rice husk

Sample	S_{BET} (m^2/g)	Pore volume (cm^2/g)	Average pore diameter (Å)
CRH	253.4	0.17	26.2

4.4.3 Fourier Transform Infrared (FTIR)

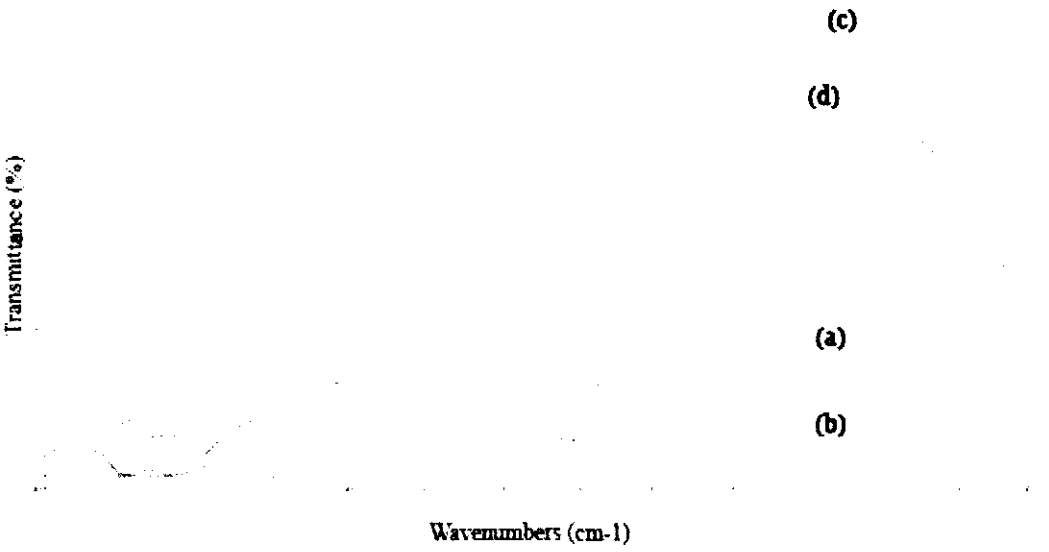

Figure 8: FTIR spectra of samples: (a) RRH, (b) TRH, (c) CRH, (d) Commercialized Activated Carbon

The FTIR technique is an important tool to identify the characteristic functional groups. FTIR provides information on the functional groups of rice husk samples and commercial activated carbon (powder) analyzed. By referring to Figure 8, both RRH and TRH samples show a wide band at about 3300-3600 cm^{-1}. The free hydroxyl group, Si-OH and O-H stretching mode of hexagonal groups and adsorbed water can be assigned to that band. The position and asymmetry of this band at lower wave numbers indicate the presence of strong hydrogen bonds.

A very small peak near 1638 cm^{-1} is attributed to the C=O stretching vibrations that may be attributed to the hemicelluloses and lignin aromatic groups. The weak intensity of this peak for all the carbon samples indicated that the raw, treated and carbonized rice husk contain a small amount of carboxyl group. Another small peak at 1550 cm^{-1} can be assigned to the C=C stretching vibration that shows indication of alkenes and aromatic functional group.

Figure 8(c) and (d) show identical spectrum. This can be concluded that carbonized rice husk has similar spectrum with commercialized activated carbon

(powder form). After carbonization of treated rice husk in a N_2 atmosphere, the spectrum of CRH sample was different from RRH and TRH. This could be due to many bands that were disappeared, which indicated the vaporization of organic matter. The changes showed evidence of the formation of structures containing multiple carbon-carbon bonds as well as the elimination of originally present oxygen and hydrogen atoms (Chen et al., 2011). Thus, carbonization helps to produce higher carbon content in the carbonized rice husk.

4.4.4 CHN Elemental Analyzer

Three samples were analyzed using CHN Elemental Analyzer which are raw rice husk, rice husk treated with 1.0 M sodium hydroxide, and carbonized rice husk at 650°C. Results of CHN analysis of each sample were presented in Table 12.

Table 12: Table of CHN analysis result

			Weight %		
No.	**Sample Name**	**Label**	**Carbon**	**Hydrogen**	**Nitrogen**
1.	Raw Rice Husk	RRH	35.13	5.728	1.22
2.	Treated Rice Husk	TRH	37.50	5.358	0.67
3.	Carbonized Rice Husk	CRH	44.53	1.648	0.98

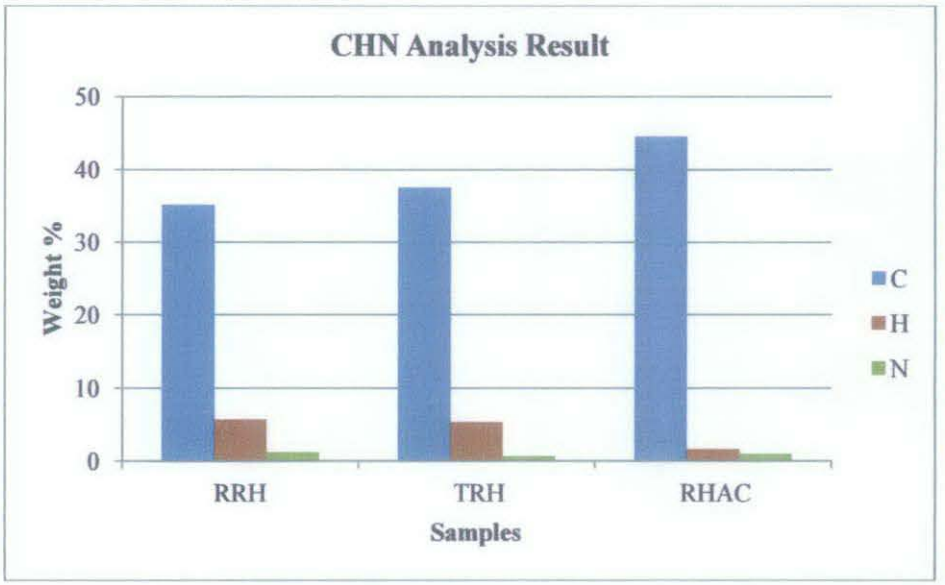

Figure 9: Graph of CHN analysis result

Based on the results obtained, it can be observed that the percentage of carbon element increased after treatment with 1.0 M NaOH and carbonized at temperature of 650°C. However, opposite trend can be observed for the weight percentage of hydrogen and nitrogen. The decreased in both elements occurred throughout the process of treatment and carbonization, thus this would increase the weight percent of carbon.

4.4.5 X-ray Diffraction (XRD)

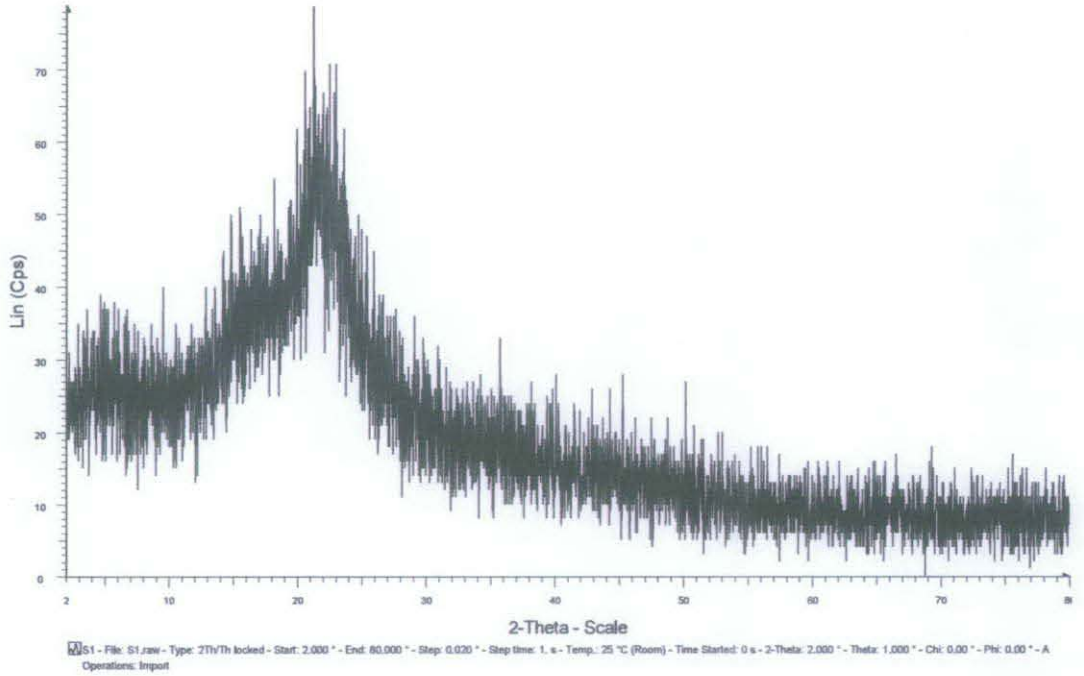

Figure 10: XRD curve of raw rice husk (RRH)

Figure 10 shows the XRD curve for raw rice husk (RRH) while Figure 11 shows the XRD curve for treated rice husk (TRH). Based on the results obtained for both RRH and TRH, it can be seen that both exhibited different curves. Generally, for XRD analysis, the crystallinity parts gave sharp narrow diffraction peaks and the amorphous component gave a very broad peak (halo). RRH sample indicated the presence of completely amorphous silica by the appearance of a broad peak centered at the 2θ angle of 22°. The appearance of both broad and sharp peak centered around 2θ = 16.5° and 22° respectively in XRD curve of TRH indicated that it had a mixture

of amorphous and crystalline phases of silica. The crystalline phases of silica are identified as crystobalite and tridymite (Chen et al., 2011).

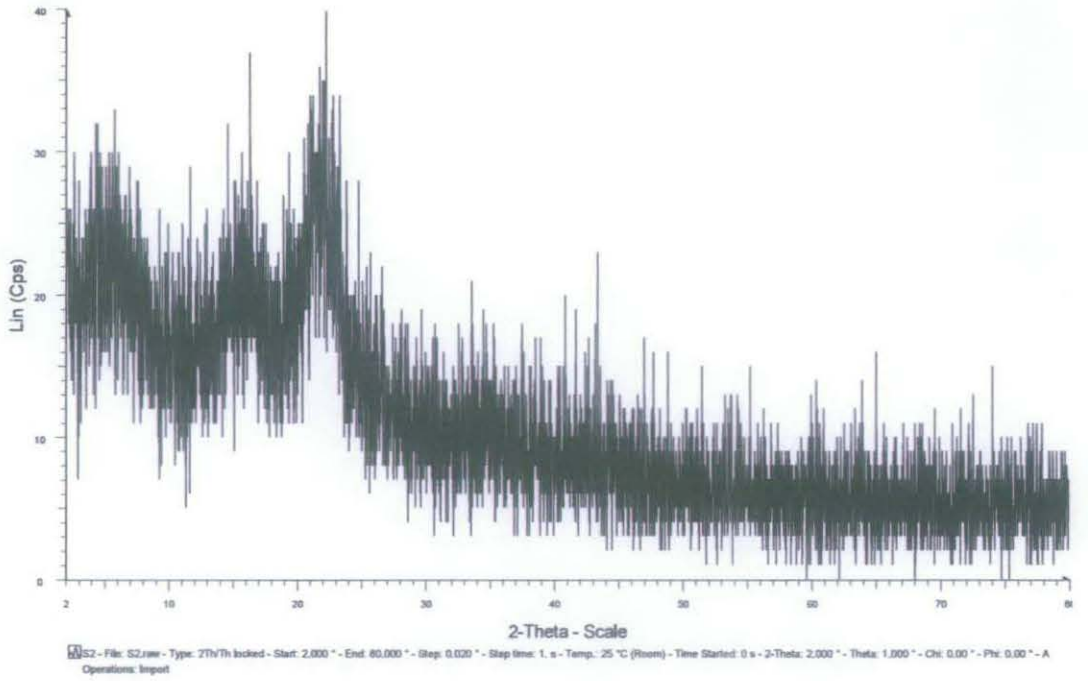

Figure 11: XRD curve of treated rice husk (TRH)

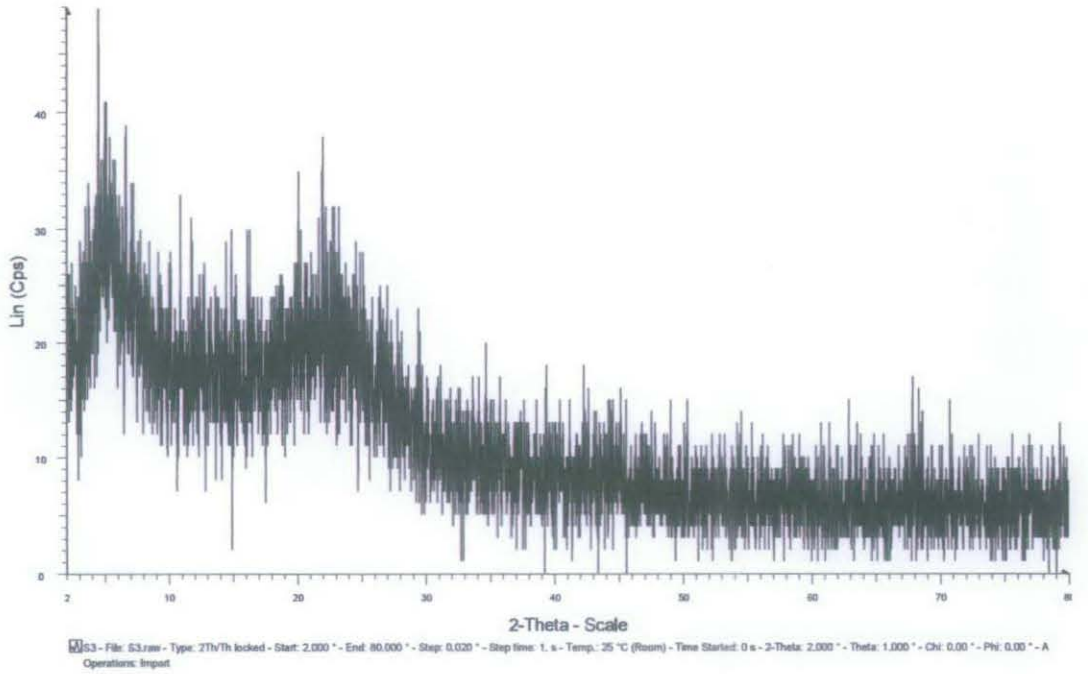

Figure 12: XRD curve of carbonize rice husk

4.4.6 Energy-Dispersive X-ray Spectroscopy (EDX)

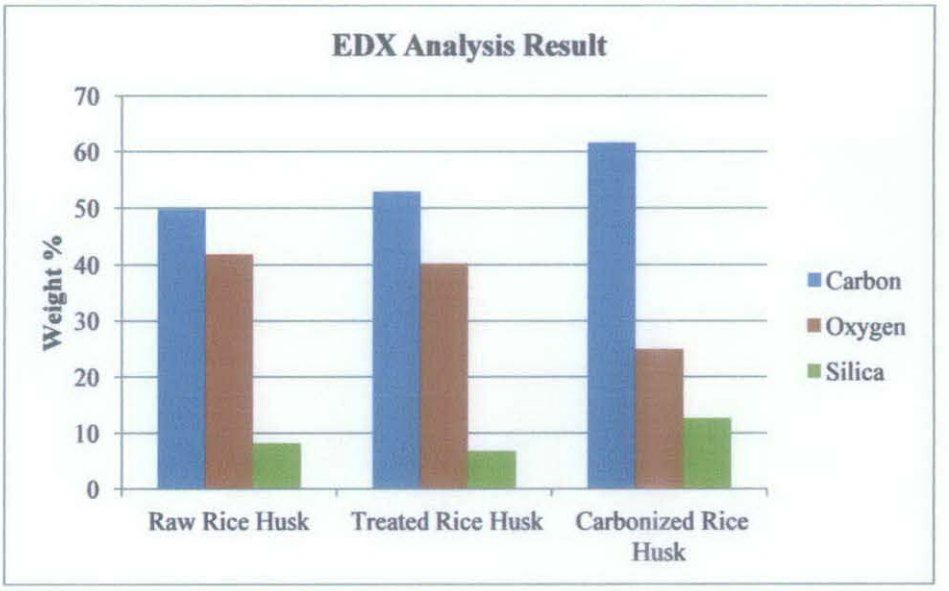

Figure 13: Graph of EDX analysis result

Figure 13 reveals changes in main components of the three samples analyzed. Generally, treatment of rice husk with NaOH and carbonization at temperature of 650°C increased the amount of carbon but reduced in the amount of oxygen. The silica content reduced after treatment with 1.0 M NaOH as compared to raw rice husk. This could be due to leaching of silica; the most abundant inorganic element in rice husk, from the external epidermis of the structure of the husk when rice husk is treated with solution of NaOH. Reaction of silica with NaOH forming sodium silicate (Na_2SiO_3) which can be easily removed by washing with water due to it solubility in water (Rahman, Saad, Shaidan & Sya Rizal, 2005). However, there was slight increment in silica content after the carbonization process (Daffalla et al, 2010).

4.4.7 Atomic Absorption Spectrophotometer (AAS)

The solution of Zn(II) ions turned from colourless to black when rice husk activated carbon (RHAC) were put into the solution shaking process. After filtering the solution, filtrate solution was analyzed using Atomic Absorption Spectrophotometer (AAS) to check the final concentration of Zn(II) ion. Standard solution of Zn(II) ions with different concentrations were prepared in order to obtain the calibration curve. Figure 10 shows the calibration curve obtained by preparation of standard solution at 0, 0.2, 0.4, and 0.8 ppm.

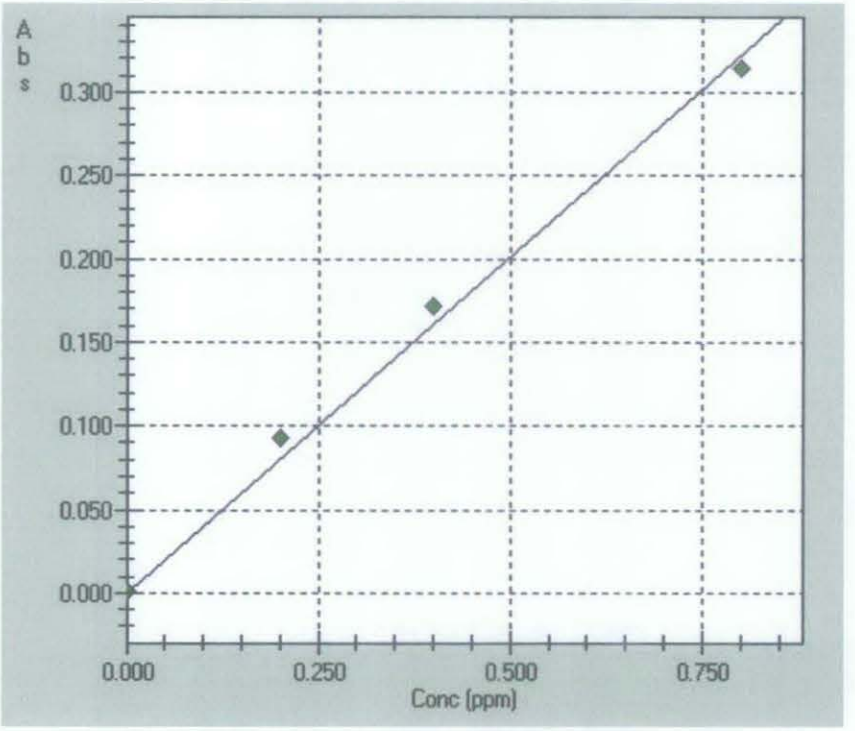

Figure 14: AAS calibration curve with $R^2 = 0.9982$

From the graph shown above, the value of R^2 represents the deviation of the data collected compared to the straight line (linear). The value of R^2 obtained from the graph was 0.9982 indicating that the standard solution prepared was considerably good as its value was close to 1.

4.5 ADSORPTION STUDY

The results of adsorption study obtained from AAS are presented in this section. Adsorption study was conducted at varied contact time (5, 15, 30, 45, 60, 90, 120, 150, and 180 minutes). Contact time mentioned here is referred to the duration of adsorbent mixed and left in the solution of adsorbate. In this study, adsorbent was referred to the activated carbon and Zn(II) as the adsorbate. The contact time is the duration of 0.1g of RHAC mixed with 15ml of 100 ppm of Zn(II) ion solution left in the stem block.

Table 13: Experimental data for effect of contact time

Adsorption Contact Time (min)	Initial Concentration, Co (ppm)	Final Concentration, Ce (ppm)	Percent Metal Uptake (% removal)	Adsorption Capacity, (mg Zn(II) ion adsorbed/ g adsorbent)
5	100	3.13	96.87	14.53
15	100	3.13	96.87	14.53
30	100	3.08	96.92	14.54
45	100	3.07	96.93	14.54
60	100	3.08	96.92	14.54
90	100	3.08	96.92	14.54
120	100	3.07	96.93	14.54
150	100	3.07	96.93	14.54
180	100	3.07	96.93	14.54

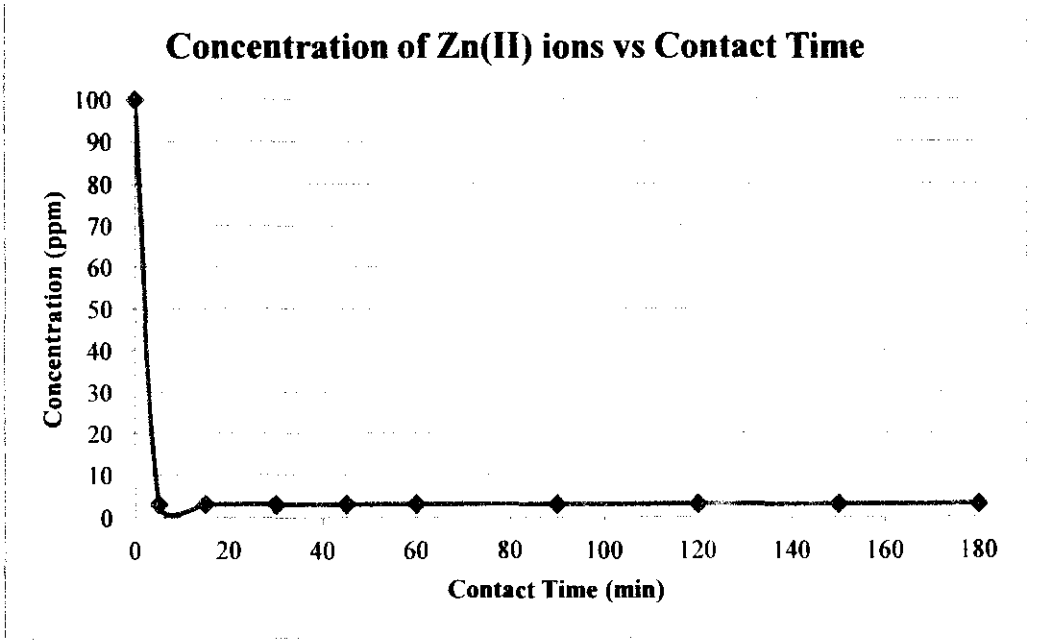

Figure 15: Effect of contact time on concentration of Zn(II) ion solution

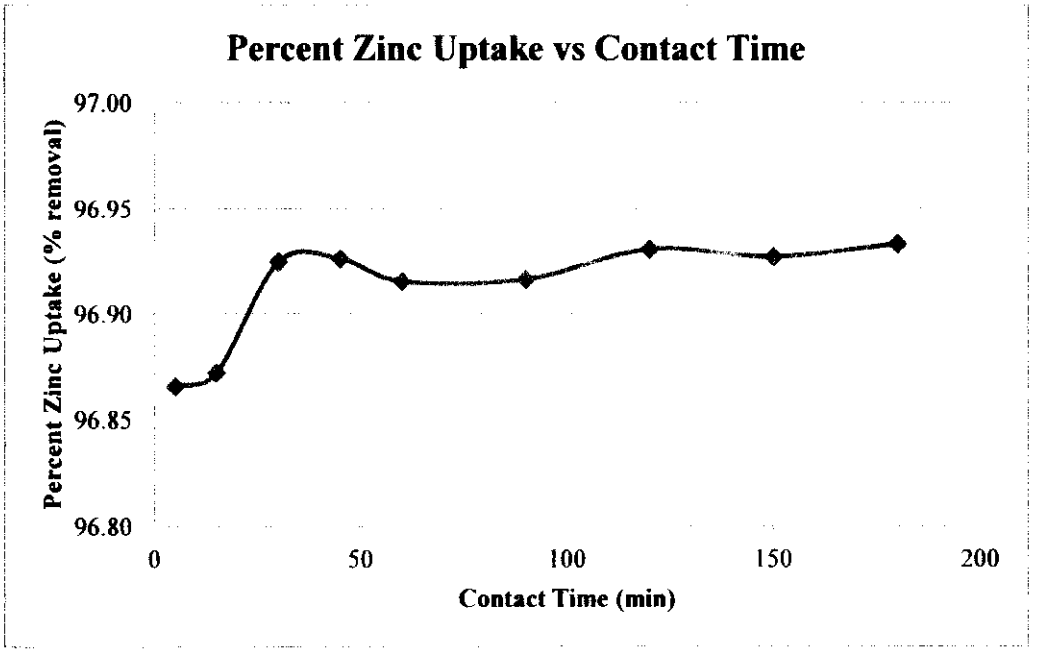

Figure 16: Effect of contact time on percent zinc uptake

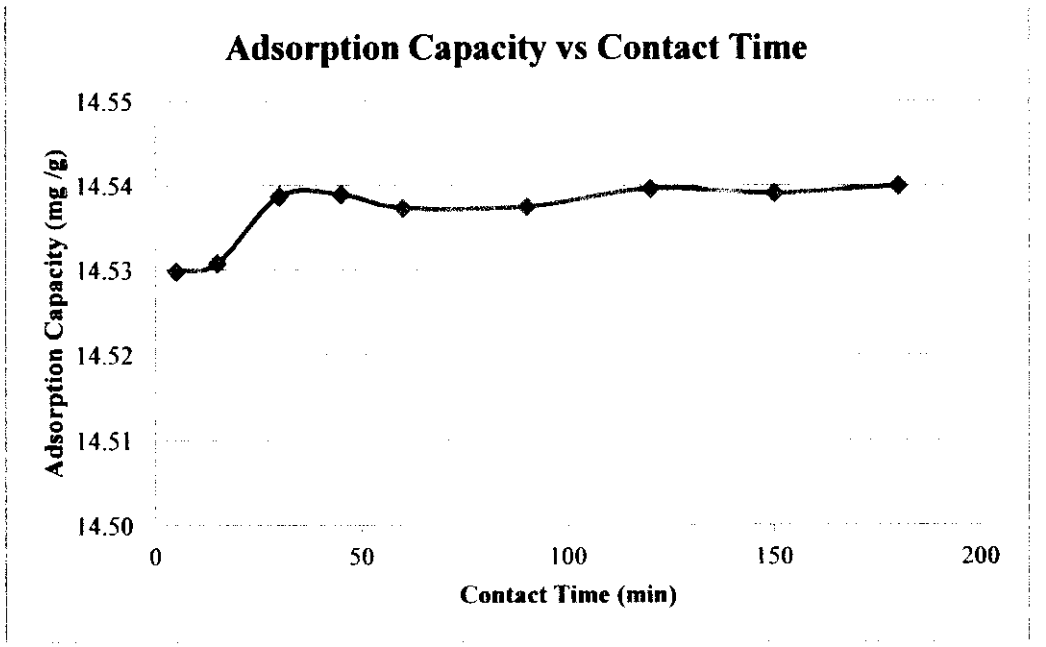

Figure 17: Effect of contact time on adsorption capacity

Figures 16 and 17 show the percent zinc uptake and adsorption capacity for rice husk carbonized at 650°C and at varied contact time. Based on the results obtained, it was observed that the percent zinc uptake and adsorption capacity increased as adsorption contact time increased, until the system reached equilibrium. Although there was fluctuation, most likely it occurred because of slight error in measurement of preparation for batch adsorption study. As shown in Figures 16 and 17, the rate of adsorption was fast in the initial stage and only slight changes in the extent of adsorption was observed after the system reached equilibrium.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 CONLUSIONS

Based on the results obtained throughout the study, several conclusions can be made as the followings:

1. The pores of rice husk are developed through chemical treatment with sodium hydroxide and carbonization process; and highly porous rice husk based activated carbon with high adsorption capacity was produced.
2. Adsorption of Zn(II) ion increases as the contact time increases, until equilibrium reached.
3. Abundant availability of rice husk have the potential as low-cost adsorbent for removal of Zn(II) ion from aqueous solution and can be utilized for wastewater treatment.

5.2 RECOMMENDATIONS

After the study has been completed, several recommendations have been identified to further improve the current research. The recommendations are listed below.

1. To study deeper on the surface area, pore sizes and pore volumes of the sample using Brunauer-Emmet-Teller (BET) method. By obtaining BET results, the relation between adsorption of Zn(II) ion by rice husks and the surface properties can be justified. RHAC sample that will be sent for BET analysis also need to be in condition and have not yet been exposed to the environment for a long time. Recommended degassing temperature is above 250 °C.
2. Performing TGA analysis with testing time at least more than 1 ½ hour in order to obtain straight line towards the end of TG thermogram, which used to determine the weight percent of ash content.
3. To study the effect of solution pH on adsorption activities.
4. To study the effect of initial concentration of aqueous solution on adsorption activities by varying initial concentration of Zn(II) ions solution.
5. Batch study for different solution concentration, so that isotherm model (Langmuir and Freundlich) can be studied. Recommended concentration is below 100 ppm (75 ppm, 50 ppm, 25 ppm) due to limitation of AAS that only can read Zn(II) ions concentration maximum at 4 ppm (provided that future study follows same methodology).
6. Speed up the preparation process by using more advance equipments especially for grinding and sieving process that can take a lot of time due to limitation of equipments used in this study.
7. To investigate the adsorption activities using other metals such as Pb and Ni.

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APENDICES

APPENDIX I

Preparation of 1.0 M of NaOH from NaOH pellets

Molar mass of NaOH = 39.9971 g/mol ~ 40 g/mol

To prepare 1.0 M of NaOH in 1 L volumetric flask, we need 40 g of NaOH pellet to be diluted in 1.0 L of distilled water.

$$Weight\ of\ NaOH\ pellet\ needed = 40\ \frac{g}{mol} \times \frac{1\ mol}{1\ L} \times 1\ L$$

$$= \mathbf{40\ g}$$

APPENDIX II

Calculation of 100 ppm of Zn(II) ions solution

In order to minimize error, the solution prepared is started from 500 ppm $ZnCl_2$;

$$500\ ppm\ by\ mass = \frac{500\ mg\ Zn(II)}{1\ kg\ of\ water}$$

Given the molar mass: Zn – 65.38 g/mol; $ZnCl_2$ – 136.28 g/mol

Assuming 1.0 mol of $ZnCl_2$, thus having 1.0 mol of Zn(II)

$$Mass\ of\ Zn(II)\ ions = \frac{65.38\ g\ Zn(II)}{1\ mol\ of\ Zn(II)} \times 1\ mol\ of\ Zn(II)$$

$$= 65.38\ g\ Zn(II)$$

$$Mass\ of\ ZnCl_2 = \frac{136.28\ g\ ZnCl_2}{1\ mol\ of\ ZnCl_2} \times 1\ mol\ of\ ZnCl_2$$

$$= 136.28\ g\ ZnCl_2$$

$$Percent\ mass\ of\ Zn(II) = \frac{65.38\ g\ Zn(II)}{136.28\ g\ ZnCl_2} = \frac{0.4797\ g\ Zn(II)}{1.000\ g\ ZnCl_2}$$

Then, 500 mg of Zn(II) ions in $ZnCl_2$;

$$500 \times 10^{-3} g\ of\ Zn(II) \times \frac{0.4797\ g\ Zn(II)}{1.000\ g\ ZnCl_2} = 1.042\ g\ of\ ZnCl_2$$

By using dilution formula, $\mathbf{M_1V_1 = M_2V_2}$

$$500V_1 = 100(250ml) \rightarrow V_1 = 50ml$$

Therefore, **50 ml of 500 ppm of Zn(II) ions solution** is diluted to prepare 100 ppm of Zn(II) ions.

APPENDIX III

Calculation of Percent Metal Uptake

The calculation for metal uptake is such as below:

$$\frac{Initial\ concentration - Final\ concentration}{Initial\ concentration} \times 100\%$$

For example, the initial concentration is 100 ppm and the final concentration is 2.45 ppm, therefore the percent metal uptake is;

$$\frac{100\ ppm - 2.45\ ppm}{100\ ppm} \times 100\%$$

= 97.55 % metal ion uptake

Calculation for Adsorption Capacity

The calculation for adsorption capacity is such as below:

$$\frac{Initial\ concentration - Final\ concentration}{Weight\ of\ rice\ husk\ (g)} \times Volume\ of\ solution\ (L)$$

For example, the initial concentration is 100 ppm and the final concentration is 2.45 ppm, volume of solution is 0.015 L and weight of the rice husk activated carbon used is 0.1 g, therefore the adsorption capacity is;

$$\frac{100\ ppm - 2.45\ ppm}{0.1\ g\ rice\ husk} \times 0.015\ L$$

= 14.63 mg Zn(II)/g rice husk

APPENDIX IV

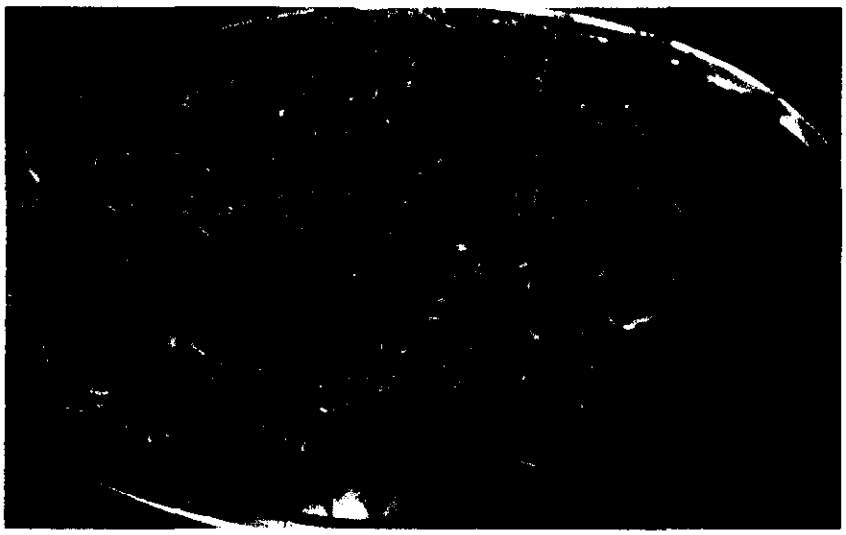

Figure 18: Raw rice husk

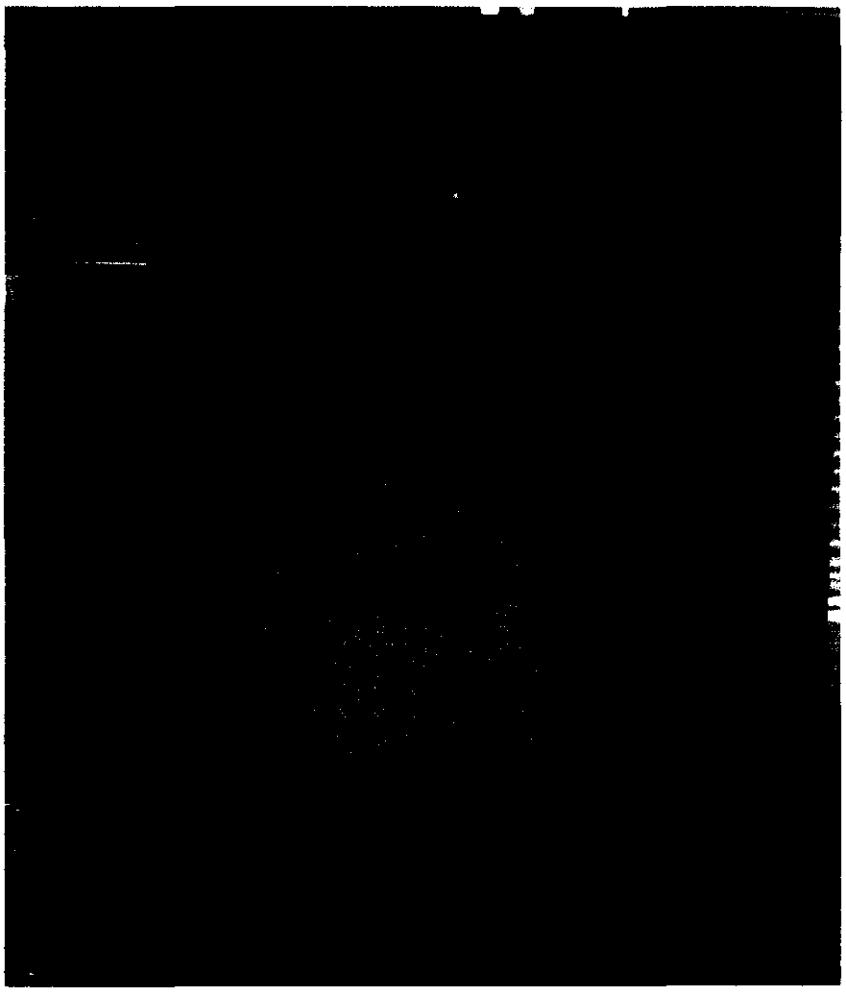

Figure 19: Oven used to dry rice husk sample

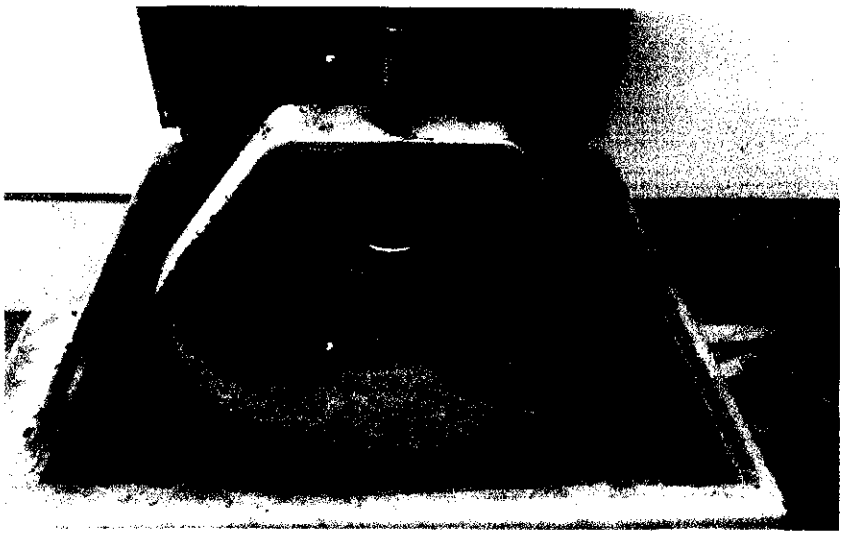

Figure 20: Mortar grinder used for grinding rice husk

Figure 21: Electrical sieve

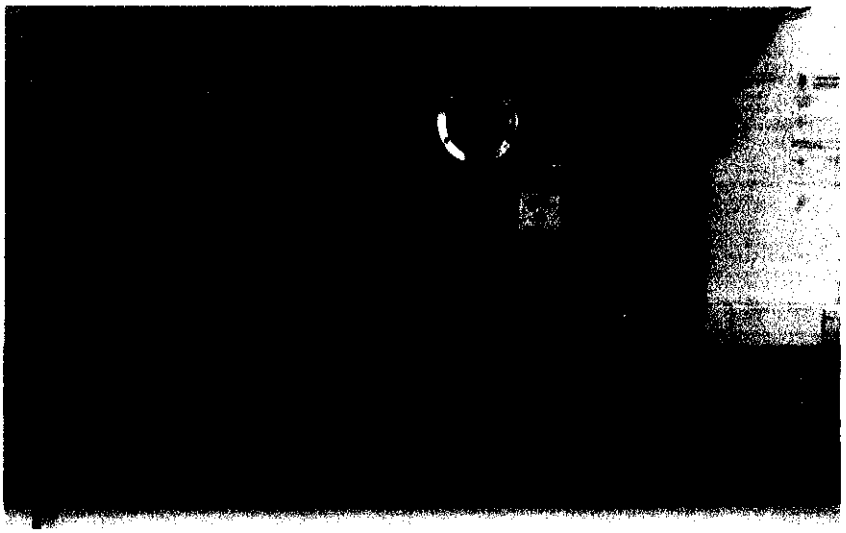

Figure 22: Furnace used for carbonization process

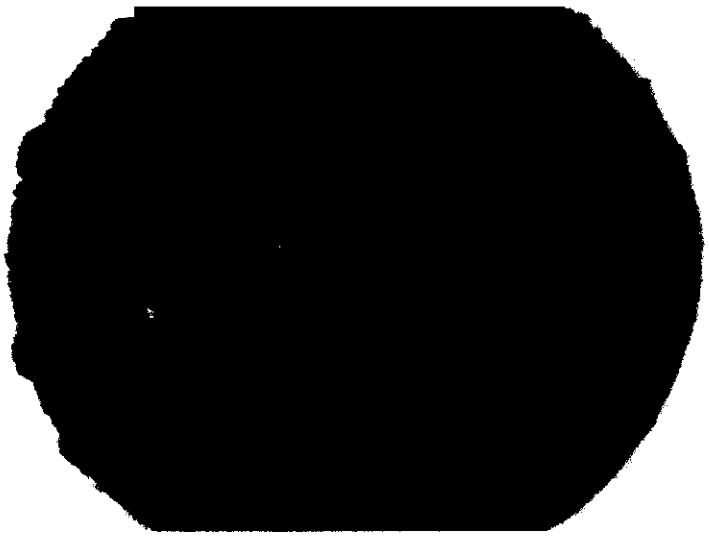

Figure 23: Carbonized rice husk

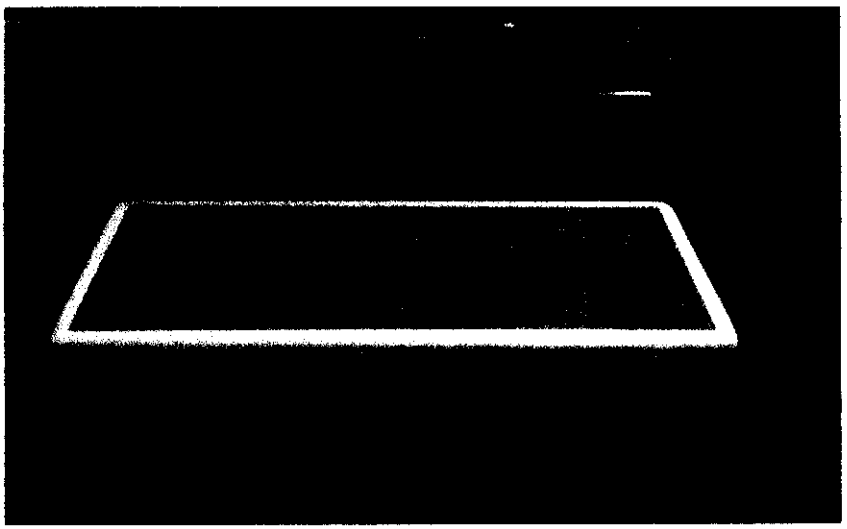

Figure 24: Adsorption study conducted using stem block